

Hydrogen production for fuel cells from the catalytic ethanol steam reforming

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Alumina-supported rhodium catalysts were shown to be active, selective and stable catalysts in the catalytic ethanol steam reforming when the reaction is carried out under pressure (1.1 MPa). Both the nature of the metal precursor salt, the metal loading and the reaction conditions were shown to influence the activity, the selectivity and the stability of the catalysts. Some trends observed when the reaction is carried out under moderate pressure were shown to be different from the conclusions drawn from earlier results obtained at atmospheric pressure. In fact, rhodium catalysts derived from a chlorinated metal precursor were shown to be the most active, selective and stable.

KEY WORDS: catalytic steam reforming; ethanol; fuel cells; hydrogen production; reaction under pressure; rhodium.

1. Introduction

The increasing environmental pollution problems originating from the exhaust gases emitted by internal combustion engines and the limited fossil hydrocarbon resources are some of the motivations to search for new engines and new energies. Fuel cell powered vehicles appear as good candidates to prevent the automotive pollution. This work is devoted to the study of the ethanol catalytic steam reforming reaction for the on-board hydrogen production for fuel cells. Ethanol was chosen as a fuel because it is environmentally friendly, renewable, CO₂-neutral, less toxic than methanol and so easier to handle, to store and to transport. Steam reforming was first developed in 1926 [1] and subsequently studied by many authors [2–4]. Previous studies, carried out with a stoichiometric mixture at atmospheric pressure, showed that alumina-supported rhodium catalysts were the most active catalysts in the ethanol catalytic steam reforming reaction [5]. At first, the purpose of this work was to investigate the effect of the total pressure in the reactor on (i) the thermodynamic equilibrium and (ii) the catalyst activity, selectivity and stability. In fact, to be able to purify the hydrogen produced from the reformer using a metallic membrane, one has to operate the system under pressure. Finally, in order to optimize the catalyst's formulation (i) the influence of the nature of the metal precursor salt, the metal loading and the reaction conditions on the reactivity of such catalysts as well as (ii) the stability of such catalytic formulations were also evaluated. Comparisons with earlier results, obtained at atmospheric pressure [6], will be made.

2. Experimental

Catalysts were prepared by wet impregnation at ambient temperature of γ -Al₂O₃ beads (200 m² g⁻¹, 1–2 mm in diameter) using either Rh(NO₃)₃ or RhCl₃ as a rhodium precursor. After drying overnight at 120 °C, catalysts were calcined under flowing dry air (30 mL min⁻¹) at 700 °C for 4 h.

Reactivity testing was carried out at 1.1 MPa in a tubular fixed-bed stainless steel reactor (up flow). Two hundred and fifty milligram catalyst diluted in 2.75 g carborundum (1.950 mm), reduced under flowing hydrogen (50 mL min⁻¹) at 500 °C for 15 h, were used for each run. The water to ethanol ratio was kept equal to 4, without any dilution. The gas hourly space velocity (GHSV), expressed as the catalyst volume to the inlet reactant flow rate ratio, was varied from 13,400 to 48,700 h⁻¹. Ethanol and water were introduced as liquids using a Gilson 307 pump. Each test was performed at 700 °C. The total pressure in the reactor was regulated using a Grove-type back pressure regulator. Before the gas phase analyzers, condensable vapors such as ethanol, water, ethanal, acetone... were trapped using a condenser set at 0.5 °C. Gas analysis was performed using a combination of two gas chromatographs equipped with TCD detectors and one gas chromatograph equipped with a FID detector. H₂ was analyzed using a TCD, equipped with a 5A molecular sieve column, with N₂ as both the carrier gas and the reference gas. N₂, CO, CO₂ and CH₄ were analyzed using a TCD, equipped with a CTR column (Alltech), with H₂ as both the carrier gas and the reference gas. Finally, hydrocarbons (CH₄, C₂H₆ and C₂H₄ essentially) were separated on a Porapak Q column and analyzed with the FID detector. In order to accurately quantify the different components of the gas mixture, calibrations for H₂, CO₂, N₂, CO, CH₄, C₂H₆ and C₂H₄ were regularly performed. In addition, two infrared

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specific detectors were used to check the CO and CO₂ concentrations. The liquid phase was analyzed using a ThermoFinnigan HPLC line equipped with both a UV 6000 LP photodiode detector and a RI 150 refractometer.

3. Results and discussion

In order to operate a H₂/O₂ proton exchange membrane fuel cell (PEMFC) properly, high purity hydrogen, almost CO-free, should be fed to the anode. However, the hydrogen produced from a reformer contains relatively high concentrations of carbon monoxide and several purification steps are required (HT-WGS, LT-WGS...). For the very final purification step, getting the CO level from less than 1% to traces, metallic palladium-based membranes might be used. In that case, the whole hydrogen production and purification system must be operated under pressure.

Then, the purpose of the present study was to check the feasibility of the hydrogen production from the ethanol steam reforming at 1.1 MPa.

3.1. Thermodynamic study

At first, we investigated the impact of the total pressure on the thermodynamic equilibrium. We used a homemade software to determine the equilibrium composition of the gas mixture (C₂H₅OH, H₂O, CO₂, H₂, CO, CH₄, CH₃CHO, CH₃COCH₃, C₂H₆, C₂H₄) from the minimization of the Gibbs free energy. It appears, as shown on figure 1, that an increase in the total pressure leads to a decrease in the hydrogen and carbon monoxide yields while the equilibrium composition in methane increases widely. The opposite variations of the hydrogen and methane equilibrium concentrations are directly linked. In fact, one molecule of methane "contains" two molecules of dihydrogen. Furthermore, an increase in the methane

concentration would directly negatively impact on the metallic membrane performances, with a loss in the purified hydrogen flow. Additionally, earlier thermodynamic studies [7] showed that an increase in temperature would (i) increase the H₂ and CO equilibrium concentration and (ii) decrease the CH₄ equilibrium concentration. As a result, for an optimum operation of the system, a good compromise had to be found between the overall performances of both the reformer and the metallic membrane. Such a compromise was found at 700 °C and moderate pressure, typically 1.1 MPa.

One can further conclude from these results that (i) ethanol is totally converted under such reaction conditions, (ii) no by-products formation such as ethene (ethylene), ethanal (acetaldehyde), propanone (acetone) and ethane is thermodynamically favored in that case and (iii) the equilibrium composition of the gas mixture, excluding the water (dry gases), at 700 °C and 1.1 MPa is: 58.2% H₂ + 17.1% CO₂ + 10.6% CO + 14.1% CH₄.

Secondly, to check the feasibility of the process, the performances of alumina-supported rhodium catalysts at 1.1 MPa and 700 °C in the ethanol catalytic steam reforming reaction were evaluated. Both the influence of the rhodium precursor salt (Rh(NO₃)₃ versus RhCl₃), the metal loading (0.3 versus 0.9 wt%) and the space velocity (13,400 up to 48,700 h⁻¹) on the activity, the selectivity and the stability of the catalyst were investigated.

3.2. Influence of metal precursor salt

Two γ-Al₂O₃-supported rhodium catalysts prepared by impregnation of Rh(NO₃)₃ or RhCl₃, containing 0.2 and 0.3 wt% Rh respectively, were evaluated. The results are presented in table 1 and figure 2.

The γ-Al₂O₃-supported rhodium catalyst derived from RhCl₃ is both more active and selective towards hydrogen production. Using such a precursor, one can see that:

- (i) The hydrogen yield is increased by 70% compared to Rh(NO₃)₃.
- (ii) The methane concentration is a little lower than the equilibrium concentration, which is favorable.
- (iii) The CO—CO₂ mixture is not equilibrated: the water gas shift (WGS) reaction equilibrium is not reached. In fact, this is not surprising considering the very low activity of rhodium in this reaction compared to platinum, copper... [8].
- (iv) The formation of ethane and ethene is low.

On the opposite, the use of Rh(NO₃)₃ leads to a poor catalyst with a very poor selectivity towards CO₂ formation (8.6%) and a high production of methane (21.8%). Additionally, the productions of ethane and ethene are not negligible any more.

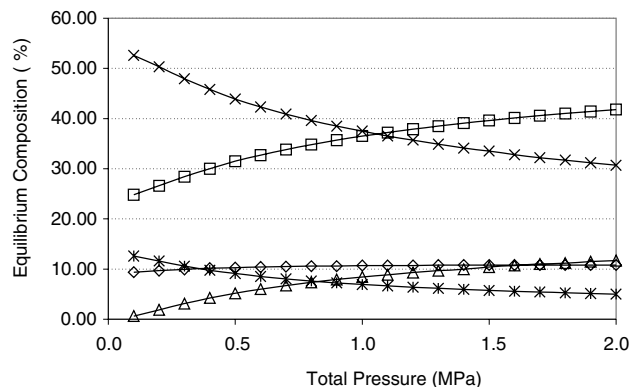


Figure 1. Evolution of the equilibrium composition in H₂ (x), CO₂ (◇), CO (*), CH₄ (Δ) and H₂O (□) as a function of the total pressure (0.1–2 MPa) in the ethanol steam reforming reaction ($T = 700$ °C, water:ethanol molar ratio = 4).

Table 1
Ethanol steam reforming ($T = 700\text{ }^{\circ}\text{C}$, $P = 1.1\text{ MPa}$, $\text{GHSV} = 24,000\text{ h}^{-1}$, water:ethanol molar ratio = 4) over $\gamma\text{-Al}_2\text{O}_3$ -supported rhodium catalysts: gas phase composition in H_2 , CO_2 , CO and CH_4 after 24 h of operation

Rhodium precursor	H_2 (%)	CO_2 (%)	CO (%)	CH_4 (%)	C_2H_4 (%)	C_2H_6 (%)	$\text{C}_2\text{H}_5\text{OH}$ conv. (%)	H_2 yield ($\text{g h}^{-1}\text{ g}_{\text{cat}}^{-1}$)
$\text{Rh}(\text{NO}_3)_3$	42.7	8.6	22.4	21.8	0.6	3.8	99.5	1.0
RhCl_3	59.6	14.6	11.7	14	0	0.1	99.9	1.7

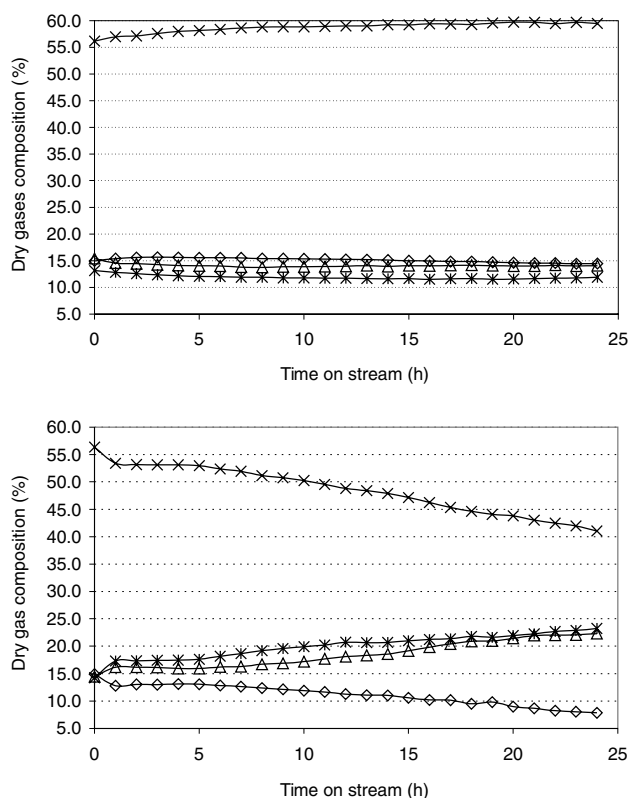


Figure 2. Ethanol steam reforming ($T = 700\text{ }^{\circ}\text{C}$, $P = 1.1\text{ MPa}$, $\text{GHSV} = 24,000\text{ h}^{-1}$, water:ethanol molar ratio = 4) over $\gamma\text{-Al}_2\text{O}_3$ -supported rhodium catalysts: evolution as a function of time on stream of the gas phase composition in H_2 (x), CO_2 (\diamond), CO (*) and CH_4 (\triangle).

Looking at the stability of these catalysts, it clearly appears from figure 2 that RhCl_3 derived catalysts should be preferred. In fact, upon 24 h of operation, such catalysts tends to activate as a function of time on stream while $\text{Rh}(\text{NO}_3)_3$ derived catalysts drastically deactivate. This deactivation occurs with:

- A rapid decrease in the hydrogen yield from 1.8 to $1.0\text{ g h}^{-1}\text{ g}_{\text{cat}}^{-1}$.
- A degradation, from 13.2 to 8.6% , of the selectivity towards CO_2 formation. In fact, such a catalyst is clearly not able to equilibrate the $\text{CO}\text{--}\text{CO}_2$ mixture.
- An increase in the production of methane from 14.4 to 22.3% .

- An increased formation of ethene from 0.3 to 4.4% . Such a product might be responsible for the deactivation as it might polymerize and block the active sites on the surface (coke formation).

These observations totally differs from what was observed at atmospheric pressure on the same type of catalysts [6]. In fact, at atmospheric pressure (0.1 MPa), chlorine-free precursors would be preferred. One explanation for this difference could be the impact on the catalyst activity and selectivity of the surface acidity. In fact, chlorine would remain on the catalyst surface when the reaction is run at atmospheric pressure while chlorine might be easily eliminated from the support surface under high partial pressure in water at elevated temperature. So that, under 1.1 MPa , $0.3\text{ wt}\%$ $\text{Rh}(\text{ex-RhCl}_3)/\gamma\text{-Al}_2\text{O}_3$ would be almost fully dechlorinated. Such a catalyst would behave as a chlorine-free catalyst, with no more surface acidity induced by the presence of chlorine.

3.3. Influence of the metal loading

Two $\gamma\text{-Al}_2\text{O}_3$ -supported rhodium catalysts prepared by impregnation of RhCl_3 , containing 0.3 and $0.9\text{ wt}\%$ Rh respectively, were compared. The results are presented in Table 2.

As we increased the rhodium loading, we observed that the overall activity of the catalyst was improved. In fact, there might be two reasons for that:

- The catalyst is more active in the methane catalytic steam reforming and some “additional” dihydrogen is produced.
- The catalyst also has a higher activity in the WGS reaction and upon CO conversion to CO_2 some dihydrogen is formed from the water. This explanation is consistent with the very low activity of metallic rhodium in the WGS reaction [8]. This is also in agreement with earlier results obtained at atmospheric pressure demonstrating that the $\text{CO}\text{--}\text{CO}_2$ “balance” is controlled by the water gas shift reaction [5].

As a result, the gas mixture composition after reaction over $0.9\text{ wt}\%$ $\text{Rh}(\text{ex-RhCl}_3)/\gamma\text{-Al}_2\text{O}_3$ is very close to the one predicted from the thermodynamic equilibrium.

Table 2

Ethanol steam reforming ($T = 700\text{ }^{\circ}\text{C}$, $P = 1.1\text{ MPa}$, GHSV = $24,000\text{ h}^{-1}$, water:ethanol molar ratio = 4) over $\gamma\text{-Al}_2\text{O}_3$ -supported rhodium catalysts: gas phase composition in H_2 , CO_2 , CO and CH_4 after 5 and 24 h of operation

Metal loading (wt %)	t (h)	H_2 (%)	CO_2 (%)	CO (%)	CH_4 (%)	$\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$ (%)	$\text{C}_2\text{H}_5\text{OH}$ conv. (%)	H_2 yield ($\text{g h}^{-1} \text{ g}_{\text{cat}}^{-1}$)
0.3	5	57.3	15.5	12.5	14.4	0.2	99.9	1.6
	24	59.6	14.6	11.7	14	0.1	99.9	1.7
0.9	5	60.1	16.8	10.4	12.2	0.4	99.1	2.2
	24	60.7	16.5	10.3	12.2	0.3	99.1	2.2

Table 3

Ethanol steam reforming ($T = 700\text{ }^{\circ}\text{C}$, $P = 1.1\text{ MPa}$, GHSV = $24,000\text{ h}^{-1}$, water:ethanol molar ratio = 4) over 0.9 wt% Rh(ex-RhCl₃)/ $\gamma\text{-Al}_2\text{O}_3$: evolution as a function of the GHSV of the gas phase composition in H_2 , CO_2 , CO and CH_4 after 5 and 24 h of operation

GHSV (h^{-1})	t (h)	H_2 (%)	CO_2 (%)	CO (%)	CH_4 (%)	$\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$ (%)	$\text{C}_2\text{H}_5\text{OH}$ conv. (%)	H_2 yield ($\text{g h}^{-1} \text{ g}_{\text{cat}}^{-1}$)
24,000	5	60.1	16.8	10.4	12.2	0.4	99.1	2.2
	24	60.7	16.5	10.3	12.2	0.3	99.1	2.2
48,000	5	58.4	15.3	11.4	14.3	0.5	99.2	4.1
	24	57.5	14.3	12.6	15.2	0.4	99.5	4.1

Furthermore, 0.9 wt% Rh(ex-RhCl₃)/ $\gamma\text{-Al}_2\text{O}_3$ exhibited an excellent stability at least up to 24 h operation. In fact, no variation in the gas phase composition is observed.

3.4. Influence of the contact time

A $\gamma\text{-Al}_2\text{O}_3$ -supported rhodium catalysts prepared by impregnation of RhCl₃, containing 0.9 wt% Rh, was tested at two different contact time by increasing the inlet flow rate by a factor of two. The results are presented in Table 3.

First of all, one can see that (i) the hydrogen concentration in the outlet gas feed is almost constant whatever the contact time and (ii) the hydrogen yield is almost doubled when the inlet gas flow rate is doubled. These observations seem to indicate that the reaction is operated under chemical control.

Furthermore, going from 24,000 to 48,000 h^{-1} , that is decreasing the contact time:

- The activity of the catalyst in the methane steam reforming reaction is decreased and more methane is detected at the reactor outlet.
- The activity of the catalyst in the WGS reaction is reduced and the CO—CO₂ mixture is not equilibrated due to the very low activity of rhodium in the WGS reaction.
- Some intermediary products, such as C_2H_4 and C_2H_6 , do not react and appear in the outlet gas phase. In fact, ethene is considered as one of the primary product in the ethanol transformation [9]. Ethene is obtained from the ethanol dehydration reaction on acidic sites on the support.

(iv) Some little deactivation is observed as a probable consequence of the formation of coke on the catalyst surface by ethene polymerization.

(v) Finally, as a primary product in the ethanol transformation, ethanal is also formed [9]. As the contact time decreased, we observed an increase by one order of magnitude in the outlet concentration in ethanal from 4.0×10^{-5} to $5.4 \times 10^{-4} \text{ mol h}^{-1}$.

As a conclusion one can state that the catalyst selectivity towards CO₂ formation, at low contact time, is almost controlled by the WGS reaction. To improve the catalyst performances under such operating conditions one could imagine to introduce some “additives”, such as ceria or platinum, to enhance the final selectivity of the catalysts. In fact, ceria-based oxides as well as some metals such as Pt, Cu, Zn or Fe were shown to be highly active in the WGS reaction [8,10].

For the Rh(NO₃)₃-derived catalyst, which one was not even stable at 24,000 h^{-1} (see Section 3.1, figure 2), the impact of the decrease of the contact time was dramatic. After 24 h operation, H_2 and CO₂ concentrations drop to 36.2 and 5.1% respectively while CO, CH_4 and $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$ concentrations increase to 24.4, 25 and 9.4% respectively. Furthermore, the ethanal concentration at the reactor outlet increased from $4.8 \times 10^{-6} \text{ mol h}^{-1}$ at 24,000 h^{-1} to $1.4 \times 10^{-2} \text{ mol h}^{-1}$ at 48,000 h^{-1} . Such a catalytic formulation cannot be considered for practical applications under such operating conditions.

4. Conclusions

$\gamma\text{-Al}_2\text{O}_3$ -supported rhodium catalyst prepared by wet impregnation of RhCl₃ were shown to be

highly active, selective and stable in the ethanol steam reforming reaction at 700 °C and under 1.1 MPa total pressure. Up to 4 g of dihydrogen per hour and per gram of catalyst could be produced with a high selectivity towards CO₂ formation.

This effect of the metal precursor could essentially be explained in terms of the metal phase dispersion. In fact, higher dispersion could be reached using RhCl₃ as a precursor compared to Rh(NO₃)₃. Furthermore, the higher the dispersion of the rhodium nanoparticles, the better the activity in the steam reforming reaction.

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